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Comparison of the effect of wet and dry torrefaction on chemical structure and pyrolysis behavior of corncobs

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HIGHLIGHTS

- Both wet and dry torrefaction removed hemicellulose from corncobs.
- Dry torrefaction caused more significant structural change than wet torrefaction.
- Wet torrefaction dramatically improved levoglucosan yield from fast pyrolysis.

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ABSTRACT

Wet and dry torrefaction of corncobs was conducted in high-pressure reactor and tube-type reactor, respectively. Effect of wet and dry torrefaction on chemical structure and pyrolysis behavior of corncobs was compared. The results showed that hemicellulose could be effectively removed from corncobs by torrefaction. However, dry torrefaction caused severe degradation of cellulose and the cross-linking and charring of corncobs. X-ray diffraction analysis revealed that crystallinity degree of corncobs was evidently enhanced during wet torrefaction, but reduced during dry torrefaction as raising treatment temperature. In thermogravimetric analysis, wet torrefied corncobs produced less carbonaceous residues than raw corncobs, while dry torrefied corncobs gave much more residues owing to increased content of acid insoluble lignin. Pyrolysis–gas chromatography/mass spectroscopy analysis indicated that wet torrefaction significantly promoted levoglucosan yield owing to the removal of alkali metals. Therefore, wet torrefaction can be considered as a more effective pretreatment method for fast pyrolysis of biomass.

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1. Introduction

The negative impact of the increasing use of limited fossil fuels on environment and energy security has urged the development of green renewable energy sources (Demirbas, 2009a). Biomass has been considered as an important renewable resource for the future, which can be converted into fuels and chemical feedstock by various technologies (Demirbas, 2009b). Owing to the structural heterogeneity and low volumetric energy density of biomass, pretreatment is usually needed to improve the efficiency of its conversion into end products (Chew and Doshi, 2011). Among all kinds of pretreatment technologies including thermal, physical, chemical methods or the combination of them, thermal pretreatment is a promising pretreatment method for thermochemical conversion of biomass. Dry torrefaction as one of thermal pretreatment technologies is generally performed at temperatures varying from 200 °C to 300 °C in the absence of oxygen. By the process, a uniform solid product spoken of as torrefied biomass with low moisture content, high energy density, enhanced grindability and hydrophobic properties is obtained (Bridgeman et al., 2008; Shang et al., 2012). The torrefied biomass is generally used as a feedstock for combustion or gasification. Compared to raw biomass, torrefied biomass is more reactive, and thus the efficiency of combustion and gasification can be improved (Chen et al., 2012; Couhert et al., 2009). In addition, the chemical composition of biomass is altered due to the typically thermal degradation of hemicellulose, and the volatiles consisting of plenty of water, organic acids and other lightweight compounds are released from biomass during dry torrefaction (Chang et al., 2012; Prins et al., 2006). It is well known that the poor quality of bio-oil from fast pyrolysis of biomass is mainly attributed to the existence of plenty of water and lightweight compounds. This suggests that dry torrefaction can be used as a pretreatment method prior to fast pyrolysis to produce high quality bio-oil. Some research studies on torrefaction-aided pyrolysis have been conducted, and it has been

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found that there were some positive influences of dry torrefaction on properties of bio-oil. More stable bio-oil with reduced concentration of water and organic acids and increased concentration of phenols and anhydrosugars has been obtained from fast pyrolysis of torrefied biomass (Meng et al., 2012; Zheng et al., 2012).

Wet torrefaction, another thermal pretreatment method, which is also known as hydrothermal pretreatment, is carried out in hot compressed water where the chemical structure of biomass is disturbed and the resulting solid product is facilitated to subsequent conversion (Holopainen-Mantila et al., 2013). Compared to dry torrefaction, the reaction temperature used for wet torrefaction is relatively lower, and the pressure is the saturated water vapor pressure. In wet torrefaction process, hemicellulose in biomass can be completely solubilized into aqueous compounds, the lignin seal is broken, and cellulose is almost entirely preserved in the solid product. Cellulose in the wet torrefied biomass is more readily accessible to enzyme, and the enzymatic digestibility of cellulose is enhanced. Thus wet torrefaction is considered as an effective pretreatment technology for subsequent enzymatic hydrolysis of cellulose (Cybulska et al., 2012; Rohowsky et al., 2013; Yu et al., 2011). As a result of the remarkable reduction in reactive hemicellulose of wet torrefied biomass, wet torrefaction may be also a potential pretreatment method prior to fast pyrolysis to improve quality of bio-oil through decreasing the formation of water and lightweight compounds mainly derived from reactive hemicellulose.

Although some similar changes in properties of biomass are observed in dry and wet torrefaction, there may be some differences in chemical structure of dry and wet torrefied biomass, which will contribute to divergences of pyrolysis behavior between them. A comparison of pyrolysis behavior of dry and wet torrefied biomass with the same mass yield will help to make a choice between two pretreatment methods for pyrolysis. However, reviewing recent literatures indicates that no such a study has been reported. In the present work, wet torrefaction of corncobs was carried out in a high-pressure batch reactor (autoclave) in the temperature range of 175–185 °C for 5 min, while dry torrefaction of corncobs was performed in a tube-type reactor at 245 and 265 °C for 20 min. Chemical structure and pyrolysis behavior of wet and dry torrefied corncobs were respectively examined. A comparative study was made to clarify different effects of wet and dry torrefaction on pyrolysis behavior of corncobs.

2. Methods

2.1. Material preparation

The corncobs were purchased from Baodi feed mill in Tianjin, China. The samples were ground to pass a BS 40-mesh sieve and retained on a BS 60-mesh sieve. Then these selected particles were oven-dried at 105 °C for 6 h before torrefaction.

2.2. Torrefaction experiment

Wet torrefaction of corncobs was carried out at 175, 185, and 195 °C in a high-pressure batch reactor detailed in a previous paper (Chang et al., 2013). A mixture of corncobs and water (corncobs:water = 1:9 w/w) was put into the reactor, and then the reactor was sealed. Before heating the reactor, nitrogen gas was passed through it at a flow rate of 1 L/min for 20 min to eliminate the presence of oxygen. Then the reactor with magnetic agitator operating at 600 rpm was heated using an electric furnace up to the target temperatures within 10–15 min. When the reactor reached the reaction temperature, the electric furnace was moved away. After maintaining the reaction temperature for 5 min, the reactor was cooled quickly to <100 °C using a coolant box filled with cooling water. The wet torrefied corncobs were obtained by filtrating the reaction products including solid residue and liquid product, and washed carefully with water for several times. The solid residue was weighed after it was oven-dried at 105 °C for about 15 h.

Dry torrefaction of corncobs was conducted in a tube-type reactor made of quartz. About 2 g of samples were placed in a porcelain boat, and the loaded boat was then pushed into the center of the reactor at room temperature. The center of reactor was heated using a ribbon heater at a heating rate of 10 °C/min under the inert environment up to the desired temperature (245 and 265 °C). After 20 min of torrefaction, the boat was moved to the end of reactor for cooling the samples to the ambient temperature. Then the dry torrefied samples were recovered and weighed. The mass yield of torrefied corncobs was calculated as the dry weight of original corncobs divided by the dry weight of torrefied corncobs. Three parallel experiments were performed for each reaction temperature, and all of experimental results were found to be highly reproducible. Torrefied corncobs were kept in the airtight sample bags and stored in a desiccator for characterization of chemical structure and pyrolysis behavior later.

2.3. Chemical composition analysis of solid samples

The contents of hemicellulose, cellulose, and acid insoluble lignin in solid samples consisting of raw and torrefied corncobs were determined by the National Renewable Energy Laboratory (NREL) method (Sluiter et al., 2008b). Firstly, the extractives in the sample were removed by exhaustive water and ethanol extraction. Then approximately 0.15 g of the extractives-free sample was weighed and treated with 72% H_2SO_4 for 1 h. Subsequently, the mixture was diluted with water of 42 ml and further hydrolyzed in an autoclave at 121 °C for 1 h. The hydrolysis solution was filtered by crucibles to separate the filtrate and residue. The sugars in the filtrate were analyzed by high performance liquid chromatography (HPLC). Conversion factors were used to convert monose concentrations into the contents of cellulose and hemicellulose in the sample. The residue was dried at 105 °C for 8 h, and the residue exclusive of ash was expressed as acid insoluble lignin in the sample. The reported results of composition analysis were the average of duplicate analysis. To investigate the decomposition degree of chemical component in torrefaction, a recovery rate of chemical component in torrefied corncobs is defined as follows:

$$\text{Recovery rate}\quad(\%) = \frac{\begin{array}{c}\text{component content}\\ \text{in torrefied corncobs}\end{array}}{\begin{array}{c}\text{component content}\\ \text{in raw corncobs}\end{array}} \times \text{torrefied corncobs yield} \qquad (1)$$

2.4. Elemental analysis

The contents of organic elements including carbon, hydrogen, nitrogen, and sulfur in solid samples were determined in an elemental analyzer (Vario EL cube, elementar, Germany). The ash content of the sample was determined by NREL method (Sluiter et al., 2008a). The oxygen content on dry basis was calculated from subtracting a hundred percentage with contents of ash, carbon, hydrogen, nitrogen and sulfur.

The analyses of main metal elements in solid samples were conducted by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) (Optima 8000, PerkinElmer, U.S.A.). For ICP-OES analysis, the sample of about 0.15 g was digested for about 6 h in the 4 ml mixed acids of concentrated HNO_3 and $HClO_4$ (3:1, v/v). Then the digested sample was diluted to 10 ml with distilled-deionized water. In ICP-OES analysis, main operating conditions included nebulizer flow of 1.5 L/min, sample introduction flow of 1.5 ml/min, flush time of 10 s, delay time of 40 s, and wash time of 40 s. Five standard solutions of each metal were prepared and analyzed to generate external calibration curves for quantitative determination. Each sample was tested in triplicate for quality assurance.

2.5. Fourier transform infrared spectroscopy (FTIR) analysis

The FTIR spectra were obtained by means of a FTIR spectrometer (Nicolet 6700, Thermo Scientific, U.S.A.) between 400 and 4000 cm^{-1} with a resolution of 4 cm^{-1} and 32 scans. About 1 mg of the sample was carefully mixed with 300 mg of dry KBr and pressed into pellets. For each sample 5 spectra were accumulated and averaged. The fingerprint region in the spectra between 2000 and 500 cm^{-1} was carefully examined. Peak area and height was measured using OPUS software version 6.5 (Bruker OptIk GmbH, Ettlingen, Germany). Firstly, a straight line was drawn as the local baseline of investigated peak by connecting the lowest data point on the either side of the peak. The area above the local baseline represented the peak area and was integrated automatically by the software. The peak intensity relative to the local baseline gave peak height value. Peak area and height values for bands assigned to aromatic skeletal of lignin were divided by the values of carbohydrate reference peaks to provide relative changes in the chemical structure of corncobs in dry and wet torrefaction (Chen et al., 2010; Pandey and Pitman, 2003).

2.6. X-ray diffraction (XRD) analysis

X-ray diffractograms of solid samples were collected by an X-ray diffractometer (X'Pert Pro MPD, PANalytical B.V., Netherlands) using Cu Kα radiation ($\lambda = 0.15406$ nm) at 40 kV and 40 mA in the scanning range of 5° to 30° at a scanning rate of 2°/min with a step of 0.02°. To investigate the effect on the overall crystalline of corncobs as a result of dry and wet torrefaction, crystallinity index (CrI) and crystallite size (L_{002}) were calculated respectively using following Eqs. (2) and (3).

$$\mathrm{CrI}\ (\%) = \left(\frac{I_{002} - I_{am}}{I_{002}}\right) \times 100 \tag{2}$$

where CrI is the crystallinity index, I_{002} represents both crystalline and amorphous intensity, which is the intensity of the diffraction of (002) plane at $2\theta = 22.5°$, while I_{am} is only the intensity of amorphous region at $2\theta = 18.7°$

$$L_{002} = \frac{\kappa \times \lambda}{\beta \times \cos\theta} \tag{3}$$

where L_{002} is the crystallite size, κ is Scherrer constant (0.90), λ is the X-ray wavelength (0.15406 nm), β is the full width at half maximum (FWHM) of (002) peak, and θ is diffraction angle of (002) plane (Bhuiyan et al., 2000; Kim and Holtzapple, 2006).

2.7. Thermogravimetric (TG) analysis

TG analysis of solid samples was performed using a differential thermal analyzer (STA449F3-Jupiter, Netzsch, Germany). TG curve was acquired by heating the sample from 35 °C to 900 °C at a constant heating rate of 10 °C/min. A high-purity argon gas flow of 20 L/min was used as the purge gas to provide an inert atmosphere for TG experiment.

2.8. Pyrolysis–gas chromatography/mass spectroscopy (Py–GC/MS) analysis

Py–GC/MS experiment of solid samples was conducted at 500 °C under the helium atmosphere using a multiple-step pyrolysis instrument (Pyroprobe 5000 Series, CDS Analytical, Inc., U.S.A.) coupled to a gas chromatograph (7890A, Agilent Technologies, U.S.A.) with a mass spectrometer (5975C, Agilent Technologies, U.S.A.). In each experiment, a sample size of approximately 0.4 mg was weighed using a microbalance with an accuracy of 0.001 mg (XP6152, METTLERTOLEDO, Germany). When running a pyrolysis method by the control software in PC, the sample was heated quickly to desired temperature at a ramp rate of 10 °C/ms with a dwell time of 20 s. Subsequently, the produced pyrolysis vapor was directly swept to the injection port of the GC using high-pure helium as the carrier gas. A HP-INNOwax capillary column (Agilent 19091 N-133, 30 m × 0.25 mm, 0.25 μm film thickness) with a carrier gas flow velocity 36.4 cm/s was used for the chromatographic separation of pyrolysis products. The injector temperature was 240 °C, and a split ratio 50:1 was used. The GC oven temperature program was 2 min at 50 °C, 10 °C/min to 90 °C, 4 °C/min to120 °C, and then 8 °C/min to 230 °C with a dwell time of 29 min. The mass spectrometer was operated in an electron impact mode at 70 eV. The mass range from m/z 12 to 500 was scanned. The identification of the main peaks was made from NIST11 MS library and previously published literatures (Garcia-Perez et al., 2008).

Quantitative analysis of main pyrolysis products was made using external standard method. Five solutions of each standard compound purchased from Sigma–Aldrich were prepared by dissolving them in the GC-grade acetone. Then GC analyses of standard solutions were performed to establish the calibration curve for each standard compound. The yields of main pyrolysis products were calculated based on the dry weight of the solid sample used in pyrolysis experiment. All experimental runs were conducted three times and averaged to compensate experimental reproducibility.

3. Results and discussion

3.1. Mass yield and lignocellulosic composition of torrefied corncobs

The wet torrefied corncobs obtained from wet torrefaction at 175 °C, 185 °C, and 195 °C are respectively denoted WT-175, WT-185 and WT-195, and the dry torrefied corncobs obtained from dry torrefaction at 245 °C and 265 °C are respectively denoted DT-245 and DT-265. The mass yields of torrefied corncobs are shown in Table 1. The mass yield of wet torrefied corncobs decreases from 77.68% at 175 °C to 53.03% at 195 °C owing to the increase in torrefaction severity. Similarly, the mass yield of dry torrefied corncobs also decreases with the elevated torrefaction temperature. DT-245 with mass yield of 80.49% is comparative to WT-175 with mass yield of 77.68%, while DT-265 with mass yield of 65.78% is comparative to WT-185 with mass yield of 65.22%. The lignocellulosic compositions of torrefied corncobs are also given in Table 1. The content and recovery rate of hemicellulose in both wet and dry torrefied corncobs decrease with the increase in torrefaction temperature as can be seen in Table 1, which testifies that hemicellulose is significantly decomposed in torrefaction. Especially, DT-265 shows higher decomposition degree of hemicellulose than WT-185 with the same mass yield. The content and recovery rate of cellulose in dry torrefied corncobs also decrease when raising the torrefaction temperature, while the opposite trend can be seen for cellulose content in wet torrefied corncobs. The wet torrefied corncobs shows higher recovery rate of cellulose

Table 1
Analysis of mass yield and chemical component of torrefied corncobs (on dry basis).

Item	Corncobs	WTC-175	WTC-185	WTC-195	DTC-245	DTC-265
Mass yield (wt%)		77.68	65.22	53.03	80.49	65.78
Chemical component (wt%)[a]						
Cellulose	38.49	47.51 (95.95)	54.11 (91.68)	64.72 (89.17)	36.34 (75.99)	20.77 (52.59)
Hemicellulose	35.36	26.71 (58.67)	20.05 (36.98)	4.52 (6.78)	27.61 (62.84)	5.31 (9.88)
Acid insoluble lignin	14.34	18.09 (98.01)	20.92 (95.12)	24.39 (90.20)	23.54 (132.14)	52.25 (239.63)

[a] Value in the parentheses is the recovery rate of chemical component.

than the dry torrefied corncobs, which indicates that cellulose is less degraded in wet torrefaction than in dry torrefaction. The content of acid insoluble lignin increases with the elevated treatment temperature in both wet and dry torrefied corncobs as shown in Table 1. The dry torrefied corncobs show much higher insoluble lignin content than wet torrefied corncobs with the same mass yield, and the recovery rate of acid insoluble lignin in dry torrefied corncobs significantly increases with the rising temperature and is over 100%. This suggests that numerous new acid insoluble lignin are formed from the cross-linking and charring of cellulose and hemicellulose in dry torrefaction (Chaiwat et al., 2009; Melkior et al., 2012). Obviously, high content of acid insoluble lignin has the adverse impact on fast pyrolysis of dry torrefied corncobs. However, it appears that no new acid insoluble lignin is formed in wet torrefaction as shown by the decreased recovery rate of acid insoluble lignin in wet torrefied corncobs. This can be explained by that the cellulose structure is relatively less disrupted and probably the cross-linking and charring of cellulose less take place during wet torrefaction of corncobs. Therefore, it is concluded that the selective removal of hemicellulose from corncobs can be easier to be achieved by wet torrefaction than by dry torrefaction.

3.2. Elemental analysis

The elemental analysis of torrefied corncobs is presented in Table 2. The carbon content of dry torrefied corncobs is evidently higher that that of raw corncobs and increases as the torrefaction temperature rises. Meanwhile, the contents of hydrogen and oxygen of dry torrefied corncobs decrease when raising torrefaction temperature. This contributes to the decreased H/C and O/C ratios during dry torrefaction. Lower contents of hydrogen and oxygen in dry torrefied corncobs are probably attributed to the reduction in hydroxyl groups and other oxygenated groups (Phanphanich and Mani, 2011). However, the oxygen content of wet torrefied corncobs is enhanced compared to raw corncobs, and the increased O/C ratio is observed during wet torrefaction of corncobs. This can be explained by the increased cellulose content in wet torrefied corncobs.

Due to the concentration effect in torrefaction, the increased ash content is observed in dry torrefied corncobs as shown in Table 2. Although ash content increases with the rising temperature during wet torrefaction, the ash content of wet torrefied corncobs is lower than that of raw materials, suggesting that de-ashing process can be achieved to some extent in wet torrefaction. As a result of the de-ashing effect during wet torrefaction, the contents of main metal elements are lower in wet torrefied corncobs than that in raw corncobs as can be seen in Table 2. It is well known that a small quantity of metal elements (especially the alkali metals) in biomass will alter the pyrolysis reaction pathways of biomass constituents, resulting in the significant changes in the pyrolysis speciation and product properties. Removing the alkali metals will reduce the catalytic reaction in the fast pyrolysis of wet torrefied corncobs and enhance the yield of liquid product in fast pyrolysis (Agblevor and Besler, 1996; Yang et al., 2006).

3.3. Chemical structure analysis

FTIR provides an effective means for studying the structural changes in corncobs torrefaction. The FTIR spectra of original and torrefied corncobs between 2000 and 500 cm^{-1} region are depicted in Supplementary Fig. S1, and the spectra have been normalized to the highest peak. Some well-defined peaks are tagged in the FTIR spectra, and the assignments of these peaks are summarized in Supplementary Table S1. FTIR spectra exhibit the structural differences between original and torrefied corncobs. The intensity of the peak (1) at 1736 cm^{-1} assigned to unconjugated C=O valence vibration in acetyl of xylan (hemicellulose) decreases in WTC-185, WTC-195 and DTC-265, which indicates that the acetyl groups can be removed from corncobs by torrefaction treatment. The intensity of the peak (7) at 1254 cm^{-1} that is assigned to syringyl ring and C—O stretch in lignin and xylan decrease in WTC-195 and DTC-265, which can be explained by the significant decomposition of xylan during torrefaction. The evidently decreased intensity of the peak (11) at 899 cm^{-1} assigned to C—H deformation in cellulose in DTC-265 is attributed to the significantly decreased cellulose content in DTC-265.

To evaluate the relative changes in chemical structure of torrefied corncobs, the ratios of intensity of the peak at 1515 cm^{-1} (I_3) associated to aromatic skeletal in lignin with intensities of peaks at 1376 cm^{-1} (I_5), 1162 cm^{-1} (I_8), and 899 cm^{-1} (I_{11}) which

Table 2
Elemental analysis of torrefied corncobs (on dry basis).

Elemental analysis	Corncobs	WTC-175	WTC-185	WTC-195	DTC-245	DTC-265
C (%)	43.75	45.06	44.73	44.44	47.06	50.62
H (%)	6.38	6.59	6.42	6.24	6.01	5.63
N (%)	0.33	0.19	0.15	0.16	0.30	0.37
S (%)	0.06	–	–	–	–	–
O (%)	43.69	45.79	45.11	44.75	40.05	35.12
H/C ratio	0.146	0.146	0.144	0.140	0.128	0.111
O/C ratio	0.999	1.016	1.008	1.007	0.851	0.694
Ash (%)	5.80	2.38	3.59	4.42	6.59	8.25
Na (mg/kg)	72.85	22.19	27.10	21.07	35.45	41.80
K (mg/kg)	4893.66	112.08	109.98	138.80	8000.77	11210.05
Mg (mg/kg)	842.89	574.21	780.38	850.92	1102.28	1427.86
Al (mg/kg)	883.22	465.70	559.56	710.63	1058.47	1353.76

are indicative of carbohydrate structures are calculated and listed in Table 3. The values of I_3/I_5, I_3/I_8, and I_3/I_{11} are respectively representative of the relative intensities of aromatic skeletal vibration against C—H deformation in cellulose and hemcellulose, C–O–C vibration in cellulose and hemicellulose, and C—H deformation in cellulose. Obviously, the values of I_3/I_5, I_3/I_8, and I_3/I_{11} for DTC-265 are increased, which is indicative of the enhanced aromaticity of DTC-265, and the increased value of I_3/I_{11} further supports the fact that cellulose is significantly decomposed during dry torrefaction at 265 °C. However, the values of I_3/I_5, I_3/I_8, and I_3/I_{11} for WTC-185 with the same mass yield to DTC-265 are nearly unchanged. This implies that dry torrefaction causes more dramatic changes in chemical structure than wet torrefaction.

3.4. Crystalline analysis

Among biomass constituents, only cellulose is crystalline, while hemicellulose and lignin are both amorphous. When corncobs suffer from torrefaction treatment, crystalline changes of corncobs will take place owing to the decomposition of chemical components. Crystalline parameters consisting of crystallinity index (CrI), FWHM of (002) peak (β), and crystalline size (L_{002}) are shown in Table 4. The CrI of original corncobs is 35.19%, while the CrI of wet torrefied corncobs are higher and increase with the rise in treatment temperature from 42.98% for WTC-175 to 53.94% for WTC-195, which indicates that wet torrefaction significantly enhances the crystallinity degree of corncobs. During wet torrefaction, most of hemicellulose, part of lignin, and amorphous regions of cellulose are degraded to form the water-soluble chemicals, while most of crystalline fractions of cellulose remain intact and in the form of solid (Yu and Wu, 2010). This results in the increase in crystallinity degree of wet torrefied corncobs. Dry torrefaction can also improve the crystallinity degree as shown by the increased CrI of DTC-245, while the severe decomposition of crystalline cellulose in corncobs occurs when raising the torrefaction temperature, which causes the decrease in crystallinity degree of dry torrefied corncobs as shown by the decreased CrI of DTC-265. The FWHM of (002) peak in XRD profiles of wet torrefied corncobs decreases with the rising treatment temperature. Thus crystalline size of wet torrefied corncobs is larger than that of original corncobs according to Eq. (3) and increases with the rise in treatment temperature. Some small and less ordered cellulose crystallites with short chains that are relatively reactive may be degraded during wet torrefaction, while large and perfect cellulose crystallites that remain inert are left (Xiao et al., 2011). Therefore, the crystalline size of wet torrefied corncobs is enhanced. However, the large cellulose crystallites in corncobs may be disrupted owing to severe decomposition of cellulose during dry torrefaction at 265 °C, which contributes to the decrease in crystalline size of DTC-265.

3.5. TG analysis

The pyrolysis behavior of original and torrefied corncobs is inspected by thermogravimetric analysis. Fig. 1(a) shows weight loss (thermogravimetry, TG) curve, while Fig. 1(b) shows weight loss rate (differential thermogravimetry, DTG) curve. The characteristic parameters of thermal degradation are presented in Table 5. The evaporation of moisture for all samples is observed around 100 °C. For original corncobs, main thermal decomposition takes place as a two-step process as shown by two prominent peaks in DTG curve for original corncobs. Obviously, the thermal decomposition of reactive hemicellulose results in the formation of the first DTG peak, while the second DTG peak with the maximum weight loss rate (DTG_{max}) is induced by cellulose decomposition. The significant variation in pyrolysis behavior can be seen from DTG curve when corncobs undergo wet torrefaction. In thermal decomposition of wet torrefied corncobs, the onset temperature of devolatilization (T_i, corresponding to a weight loss of 5% respect to the final weight loss) is enhanced as shown in Table 5. The first DTG peak for hemicellulose decomposition decreases in the DTG curve for WTC-175, appears only in the form of shoulder in the DTG curve for WTC-185, and disappears in the DTG curve for WTC-195. This can be explained by the decreased hemicellulose content in wet torrefied corncobs. The maximum DTG peak for cellulose decomposition significantly increases with the elevated torrefaction temperature as shown by the increased value of DTG_{max} in Table 5, and the peak is moved to higher temperature as revealed by the enhanced value of T_{max} (temperature for the maximum rate of devolatilization). This implies that the thermal stability of wet torrefied corncobs is enhanced. As mentioned in XRD analysis, amorphous cellulose and small cellulose crystallites are removed from corncobs during wet torrefaction, while large cellulose crystallites with higher thermal stability are preserved in solid residues, and probably new hydrogen bonds between adjacent cellulose crystallites are formed which causes the formation of larger crystallite. This results in the improvement of thermal stability of wet torrefied corncobs. In the thermal decomposition of dry torrefied corncobs, the values of T_i also increase, and the DTG peak for hemicellulose decomposition nearly disappears which is

Table 3
Ratios of the intensity of the lignin-associated band with carbohydrate bands for original and torrefied corncobs.

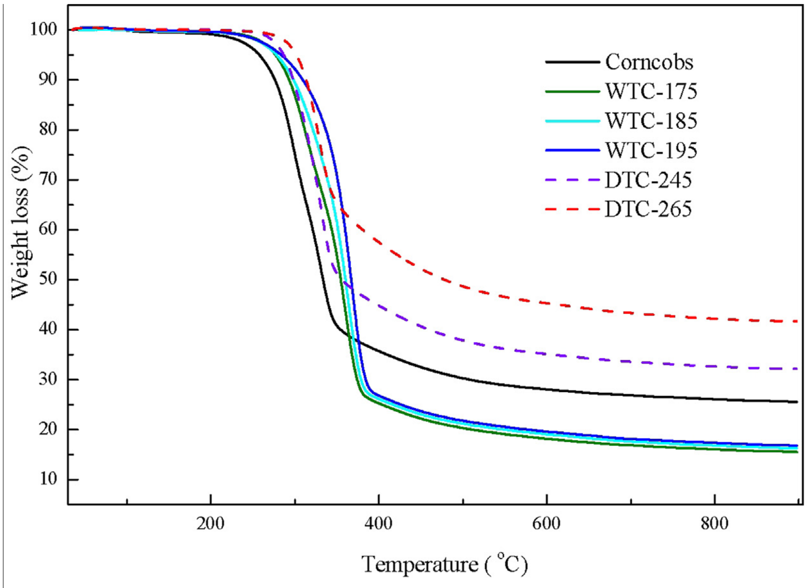
Ratio	Relative intensity of aromatic skeletal band against typical band for carbohydrates[a]					
	Corncobs	WTC-175	WTC-185	WTC-195	DTC-245	DTC-265
I_3/I_5	1.036 (1.417)	1.126 (1.500)	1.017 (1.500)	1.326 (1.611)	1.108 (1.500)	1.578 (1.967)
I_3/I_8	0.466 (0.586)	0.498 (0.553)	0.479 (0.545)	0.582 (0.679)	0.477 (0.600)	0.637 (0.690)
I_3/I_{11}	1.304 (1.308)	1.254 (1.235)	1.270 (1.200)	1.408 (1.427)	1.324 (1.364)	2.961 (2.500)

[a] The ratios are calculated using peak areas (not in parentheses) and peak heights (in parentheses).

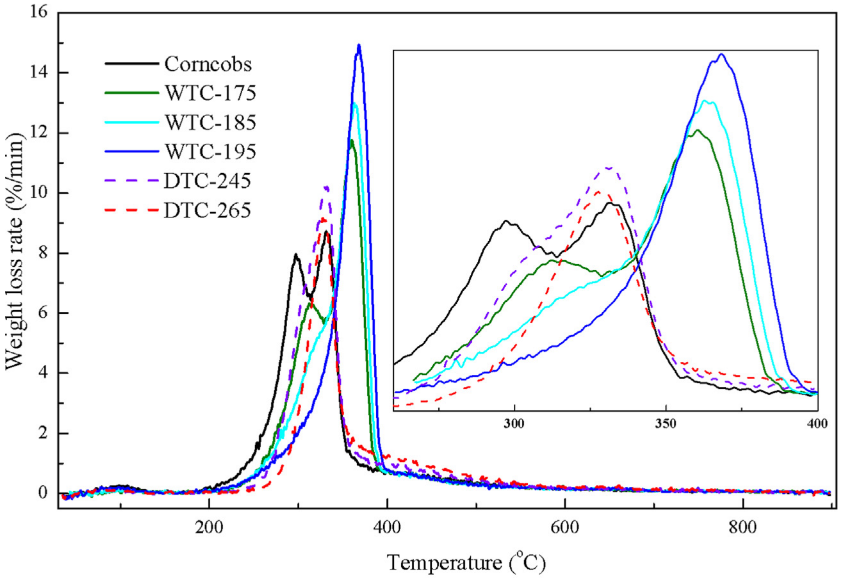
Table 4
Crystalline parameters of original and torrefied corncobs.

Parameter	Corncobs	WTC-175	WTC-185	WTC-195	DTC-245	DTC-265
CrI (%)	35.19	42.98	47.09	53.94	38.13	33.65
β[a] (degree)	2.76	2.45	2.26	1.97	2.60	2.69
L_{002} (nm)	5.77	6.51	7.08	8.12	6.13	5.93

[a] Full width at half maximum (FWHM) of (002) peak.



(a) TG



(b) DTG

Fig. 1. TG and DTG curves for raw and torrefied corncobs at the heating rate of 10 °C/min in argon atmosphere.

Table 5
Characteristic parameters from thermal degradation of original and torrefied corncobs.

Characteristic parameter	Corncobs	WTC-175	WTC-185	WTC-195	DTC-245	DTC-265
T_i (°C)	249.7	273.1	273.2	277.3	280.5	293.1
T_{max} (°C)	333.9	360.3	362.6	368.1	329.6	327.5
DTG_{max} (%/min)	8.62	11.75	12.99	14.93	10.19	9.16
Residue (%)	25.55	15.51	16.30	16.80	32.14	41.66

similar to the thermal decomposition of wet torrefied corncobs. However, the value of T_{max} slightly decreases, which suggests that the thermal stability of dry torrefied corncobs is nearly unchanged. When thermal decomposition is finished at 900 °C, carbonaceous residues for wet torrefied corncobs are lower than original corncobs, while carbonaceous residues for dry torrefied corncobs significantly increase with the rise in torrefaction temperature as shown in Table 5. This can be explained by the changed chemical composition of torrefied corncobs. The decreased residues for wet torrefied corncobs is ascribed to the increased cellulose content and decreased contents of alkali metal in wet torrefied corncobs, while the increased residues for dry torrefied corncobs is attributed to the increased contents of acid insoluble lignin and alkali metal (Raveendran et al., 1995; Wannapeera et al., 2011). It is concluded that the wet torrefied corncobs are more suitable for pyrolysis.

3.6. Py–GC/MS analysis

In Py–GC/MS experiments, fast pyrolysis process of samples can be accomplished by the micro-pyrolyzer with high heating rate, and following fast pyrolysis products are analyzed by GC/MS. Part of compounds with relatively high abundance are identified, and yields of compounds are calculated based on the dry weight of sample used in pyrolysis experiment. The quantitative analysis results are shown in Table 6.

The compounds identified consist of ketones, aldehydes, furans, organic acids, phenols, and anhydrosugars. As a result of the modified chemical structure of torrefied corncobs, some changes in pyrolysis product distribution can be seen from Table 6. The yields of nearly all ketones detected in pyrolysis of torrefied corncobs are reduced, and wet torrefied corncobs give lower yields of ketones than dry torrefied corncobs. This can partly be explained by the removal of hemicellulose from corncobs during torrefaction treatment. Acetic acid is the major organic acid with the yield of 2.85% in original corncobs pyrolysis and mainly originated from elimination reaction of acetyl groups in hemicellulose structure. The torrefied corncobs gives lower yields of acetic acid than original corncobs, and the acetic acid yield evidently decreases as torrefaction temperature rises, which is partly attributed to the removal of acetyl groups during torrefaction (Shen et al., 2010a). Hydroxyacetaldehyde (HAA) as a typical pyrolysis product derived from cellulose is the only detected aldehyde compound. The dry torrefied corncobs give lower HAA yield than original corncobs, while the wet torrefied corncobs give higher HAA yield, which can be explained by the increased cellulose content in wet torrefied corncobs. The wet torrefied corncobs produce much more 5-hydroxymethylfurfural (5-MHF) that is mainly originated from cellulose pyrolysis, while the yields of other furan compounds are reduced in pyrolysis of torrefied corncobs. A considerable number of phenols are also produced in corncobs, while torrefied corncobs, especially the dry torrefied corncobs, give lower total yield of phenols than original corncobs as can be seen in Table 6, which is attributed to the removal of some thermally unstable lignin units from corncobs during torrefaction treatment. Some anhydrosugars are detected in eucalyptus wood pyrolysis. Levoglucosan (LG) as another typical cellulose-derived pyrolysis product is one of the main anhydrosugars. Obviously, wet torrefaction significantly promotes the formation of LG as revealed by the enhanced LG yield in pyrolysis of wet torrefied corncobs, while this phenomenon cannot be observed in the pyrolysis of dry torrefied corncobs.

In general, the ring-containing products such as 5-MHF and LG are main pyrolysis products in cellulose pyrolysis. 5-MHF is generally involved in the ring-opening and rearrangement reaction, and LG is formed from the cleavage of glycosidic linkage in cellulose and subsequent intramolecular rearrangement of the formed monomer units (Shen et al., 2010b). Small amount of inorganic salts (especially alkali cations) can retard the formation of LG

Table 6
Quantitative analysis of main compounds from pyrolysis of original and torrefied corncobs.

Time (min)	Compounds	Yield (%)					
		Corncobs	WTC-175	WTC-185	WTC-195	DTC-245	DTC-265
3.33	2,3-Butanedione	0.26	0.08	0.07	0.06	0.23	0.17
8.09	Hydroxyacetone	1.36	0.56	0.58	0.60	1.19	0.91
9.10	2-Cyclopenten-1-one	0.05	0.02	0.02	0.01	0.05	0.05
9.49	1-Hydroxy-2-butanone	0.33	0.09	0.10	0.11	0.28	0.12
17.85	1,2-Cyclopentanedione	0.29	0.11	0.13	0.13	0.30	0.28
18.77	3-Methyl-1,2-cyclopentanedione	0.14	0.04	0.04	0.04	0.13	0.11
Total of ketones		2.43	0.90	0.94	0.95	2.18	1.64
8.42	Hydroxyacetaldehyde	1.17	1.80	1.89	1.89	0.92	0.75
11.47	Furfural	0.26	0.31	0.29	0.21	0.19	0.10
14.01	5-Methyl-2-furancarboxaldehyde	0.02	0.02	0.02	0.02	0.02	0.02
15.89	2-Furanmethanol	0.17	0.07	0.08	0.09	0.18	0.14
17.62	2(5H)-Furanone	0.10	0.04	0.05	0.06	0.09	0.07
22.75	5-Hydroxymethyldihydrofuran-2-one	0.32	0.14	0.14	0.15	0.25	0.16
27.13	5-Hydroxymethylfurfural	0.05	0.28	0.32	0.34	0.05	0.04
Total of furans		0.92	0.86	0.90	0.87	0.78	0.53
11.13	Acetic acid	2.85	1.63	1.52	0.84	1.67	0.97
12.70	Formic acid	0.32	0.26	0.38	0.36	0.31	0.16
13.31	Propanoic acid	0.20	0.05	0.05	0.04	0.29	0.25
15.32	Butanoic acid	0.04	0.01			0.06	0.06
Total of acids		3.41	1.95	1.95	1.24	2.33	1.44
19.28	Guaiacol	0.14	0.08	0.09	0.09	0.14	0.11
20.67	4-Methylguaiacol	0.04	0.07	0.07	0.06	0.04	0.04
21.40	Phenol	0.09	0.03	0.04	0.04	0.12	0.11
21.66	4-Ethylguaiacol	0.04	0.02	0.02	0.03	0.04	0.03
22.37	p-Cresol	0.02	0.01	0.02	0.02	0.03	0.03
23.52	4-Ethylphenol	0.03	0.01	0.01	0.02	0.04	0.03
23.75	4-Vinylguaiacol	0.43	0.36	0.36	0.30	0.19	0.08
24.53	Syringol	0.10	0.03	0.04	0.04	0.09	0.07
25.47	4-hydroxy-3-methoxybenzoic acid	0.03	0.04	0.04	0.05	0.03	0.02
25.98	2,3-Dihydro-benzofuran	0.45	0.37	0.42	0.40	0.17	0.08
27.81	Vanillin	0.10	0.06	0.08	0.04	0.01	0.01
29.84	4-Allylsyringol	0.05	0.05	0.07	0.07	0.03	0.01
Total of phenols		1.52	1.13	1.26	1.16	0.93	0.62
21.11	Levoglucosenone		0.06	0.05	0.06		
26.08	1,4:3,6-dianhydro-α-D-glucopyranose	0.19	0.18	0.19	0.20	0.22	0.23
49.02	Levoglucosan	0.43	5.30	10.97	12.13	0.45	0.45
Total of anhydrosugars		0.62	5.54	11.21	12.39	0.67	0.68

through suppressing the unzipping reaction at the free chain ends of cellulose (Patwardhan et al., 2010; Piskorz et al., 1989). Some lightweight compounds such as aldehydes and ketones could also be produced by the ring scission of cellulose itself or the formed LG. A high activation barrier exists in the ring scission of cellulose, but the ring scission of cellulose can be accelerated by direct catalysis of inorganic salts. Wet torrefaction removes alkali metals from corncobs, and the catalysis of inorganic salts can be weakened in pyrolysis of wet torrefied corncobs. In addition, the improved thermal stability of wet torrefied corncobs restrains the ring scission of cellulose, and promotes the formation of LG. Therefore, wet torrefied corncobs give much higher LG yields. In comparison of dry torrefaction, wet torrefaction is considered a more effective pretreatment method for fast pyrolysis of corncobs.

4. Conclusions

Effect of wet and dry torrefaction on chemical structure and pyrolysis behavior of corncobs was investigated. Most of hemicellulose can be removed from corncobs by torrefaction. However, dry torrefaction caused severe degradation of cellulose and cross-linking and charring of corncobs, thus more acid insoluble lignin were formed. FTIR analysis implied that dry torrefaction causes more dramatic structural change of corncobs than wet torrefaction. Py–GC/MS analysis indicated that wet torrefaction significantly improved levoglucosan yield. Therefore, from a technical point of view, wet torrefaction can be considered as a more effective pretreatment method for fast pyrolysis of corncobs.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.biortech.2014.10.157.

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